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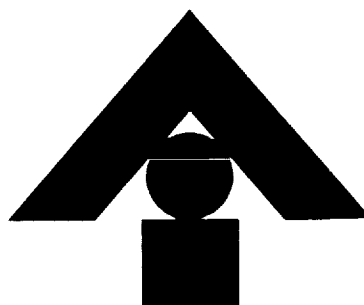
Report 108-Q1

**INVESTIGATION OF ZEOLITE
MEMBRANE ELECTROLYTES
FOR FUEL CELLS**

National Aeronautics and Space Administration
Contract NAS 7-150
Quarterly Progress Report
For Period Ending 18 September 1962

ASTROPOWER, INC.

SUBSIDIARY OF THE DOUGLAS AIRCRAFT COMPANY, INC.



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1.0 INTRODUCTION AND SUMMARY

This project is devoted to an investigation of the properties and applicability of zeolite materials as quasi-solid electrolytes in hydrogen-oxygen fuel cells. Various types of fuel cells have been constructed using aqueous solutions or fused salt as electrolytes; the use of aqueous solutions, however, has several marked disadvantages for space applications. Among these are temperature limitations, lack of zero-gravity compatibility, corrosion, need for electrolyte flow auxiliary equipment, and diffusion through the electrolyte. Such characteristics result in higher complexity and lower reliability, as well as relatively large weight and volume for a fuel cell system. These problems can be partially eliminated by utilizing an organic ion-exchange membrane as the electrolyte - for example, the General Electric fuel cell. Organic membranes, however, have some unavoidable limitations, too; in particular, they can not be used at elevated temperatures because they decompose and/or cross-link. They do not resist irradiation, they develop hot spots and cracking, they are subject to permanent damage upon drying, and they cannot (by their nature) prevent undesirable diffusion of reactants through them. If a suitable solid inorganic electrolyte could be found, the temperature limitations would be raised to considerably higher ranges, and a compact fuel cell would be obtained which would be compatible with zero gravity. In addition, the problems of drying, cracking, hot spots and short circuiting, irradiation, and diffusion could possibly be solved. Other investigators (Reference 1) also have been aware of these potential advantages and have tested various hydrated inorganic materials. However, no one has yet developed materials capable of working at elevated temperatures, due to the relatively high partial pressure of water vapor associated with hydrated compounds. The zeolites are well known for their ability to adsorb water tenaciously at very low partial pressures (Reference 2), one of their main commercial applications being the drying of various gases from traces of water. The intracrystalline water of hydration content of the zeolites, which is adsorbed inside a cavity network of a crystallite, may act as an electrolyte in a fuel cell and may be capable of functioning at higher temperatures than the organic ion exchange membranes. In a hydrogen-oxygen fuel cell the water would make possible the transport of hydrogen ions, probably in the form of hydronium ions, from the hydrogen to the oxygen electrode. This can be achieved by the hydrogen ion exchange property of zeolites. Furthermore, their molecular sieving properties can be utilized to prevent the diffusion of reactants if a suitable membrane binder is employed.

The present experimental program is designed to evaluate the potential applicability of various synthetic zeolites as hydrated solid electrolytes by investigating their physical and electrochemical properties. The crystalline zeolite powders require suitable binders to develop adequate physical strength to enable bonding into thin, 2-in. diameter disks or membranes. Techniques such as hot pressing, cold pressing, and free sintering and casting are being employed. The more suitable membranes will be assembled into thin composite wafers containing the zeolite membrane, in the middle, and powder catalysts and metal gauze electrodes on each side. The composite wafers will be quite thin (in the order of 1 to 2 mm) and could readily be stacked in series with appropriate gasketing and

gas or vapor reactant manifolds to form a compact fuel cell battery. Such an assembly would require a minimum of auxiliary equipment and moving components, and would be expected to possess higher reliability and versatility.

The physical and electrochemical properties to be investigated for the more promising membranes and composite wafers include:

- a. Physical strength
- b. Electrochemical conductivity
- c. Gas permeability
- d. Water adsorption isotherms or isosteres
- e. Hydrogen ion exchange
- f. Chemical stability

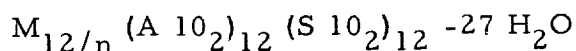
During the first quarter of this program, procedures for the initial screening tests of different zeolites and binders have been established, and apparatus has been constructed. Substantial progress has been made toward selecting a suitable binder. Inorganic phosphate binders have yielded ceramic membranes possessing promising physical strength. Measurements of the modulus of rupture indicated that zirconium phosphate-bonded zeolites produced membranes having a transverse strength in the order of 1000 psi. Preliminary tests also indicated that membranes of satisfactory physical strength could be prepared with 10 to 15% epoxy resin employed as a binder.

Additional testing of these membranes, in particular ionic conductivity and water permeability measurements, is under way. The results will be used in selecting the best membrane compositions. During the next quarter, it is planned to complete selection of the most suitable binder or binders. More attention will then be directed toward composite wafer fabrication and evaluation.

2.0 EXPERIMENTAL WORK AND DISCUSSION

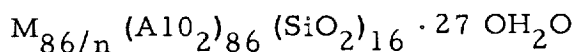
2.1 Zeolite Types Investigated

Samples of most of the commercially available synthetic zeolites have been obtained and are being evaluated. Table I gives some of the properties of the zeolites which have been received and are being investigated. The Linde Co., a Division of Union Carbide Corp., supplies the greatest variety (Reference 3). All of the Linde zeolites have crystal structures which consist essentially of hollow cubes. The internal cavities are connected through openings on each of the faces of the cube, thus giving a three-dimensional interconnected network within each zeolite crystallite. Two aluminosilicate structural arrangements are available, and the properties, especially the pore openings which admit molecules into the interior cavity network, are further varied by changing the cation associated with the aluminosilicate structure. The Linde "A" type zeolites have a cubic unit cell of 12.32 AU. The chemical composition can be represented by the formula



where M represents a univalent exchangeable cation. This type is supplied in three different cation combinations, thus yielding three different effective pore sizes of 3, 4, and 5 AU. The sodium and calcium forms are reportedly stable at temperatures up to 700°C, while the potassium form is less heat stable, the reported limit being 500°C.

The Linde "X" zeolites have the chemical composition



They crystallize into a structure having larger internal cavities and pore openings than the "A" type zeolites. They are supplied in a sodium form, pore diameter 10 AU, and a partially calcium-exchanged form with a 9 AU pore diameter. The temperature stability of the "X" zeolites is about the same as for the corresponding "A" zeolites.

Linde also supplies two other types of zeolites about which less information is available. One is designated 4A XW and reportedly is an improved form of 4A having greater bulk density and crush strength. Presumably the crystal structure and chemical properties are similar to those of 4A. The other, called AW-500, is reported to be an acid-resistant zeolite with an effective pore diameter of 4 to 5 AU. No information concerning the chemical composition or crystal structure has been made available.

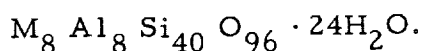
Davison Chemical Co., a division of W. R. Grace and Co., also produces zeolites under the trade name "Microtraps." It is understood that they are produced under a patent license arrangement with Linde and are essentially the same as the Linde "A" zeolites. Therefore no samples of Davison Microtraps were tested.

A new type of zeolite has been recently made available by the Norton Co. under the trade name Zeolon (Reference 4). It is a synthetic form of the mineral mordenite and has the chemical composition

TABLE I

PROPERTIES OF ZEOLITE SAMPLES TO BE INVESTIGATED

<u>Manufacturer</u>	<u>Designation</u>	<u>Cation(s)</u>	<u>Effective Pore Diameter (AU)</u>	<u>Solution Stability (pH)</u>	<u>Maximum Thermal Stability (°C)</u>
Linde	3A	70% K ⁺ , 30% Na ⁺	3	5-12	500
Linde	4A	100% Na ⁺	4	5-12	700
Linde	5A	70% Ca ⁺⁺ , 30% Na ⁺	5	5-12	700
Linde	10X	70% Ca ⁺⁺ , 30% Na ⁺	9	--	500
Linde	13X	100% Na ⁺	10	--	700
Linde	4A XW	(Improved type of 4A)			
Linde	AW-500	Not known	4-5	>2.5	500
Norton	Zeolon H	H ⁺	9-10	Acid-stable	775



It is sold in both the sodium and hydrogen ion-exchanged forms. The latter type of zeolon is reported to be acid-stable, and therefore it can be used in acidic solutions or in the recovery of acidic gases such as HCl. No manufacturer's information is available concerning water adsorption at either ambient or elevated temperatures. The mordenite crystal structure consists of chains of four- or five-membered rings constructed of tetrahedra of either aluminum or silicon, each surrounded by four oxygen atoms which are linked together to form a network that results in a system of parallel channels possessing a structure similar to a tube bundle.

2.2 Binder Types Investigated

2.2.1 Preparation Techniques

A major portion of the effort during this report period was directed toward selection of a suitable binder or binders for zeolite membrane preparation. For comparison purposes, some membranes were prepared by pressing samples of the pure zeolites at temperatures up to 150°C and pressures up to 13 tons per square inch. Frequently the membranes broke on ejection from the die; however, some were successfully removed. These membranes clearly indicated the need for a binder to impart the necessary physical strength. Selection and evaluation of binders is intimately connected with the methods used in the formation of the membranes. Various potential binders can be utilized only by certain preparative techniques.

Five different preparative techniques can be used to apply elevated temperatures and/or pressures in the formation of objects from suitable powders:

- a. Hot pressing
- b. Cold pressing and free sintering
- c. Casting and firing
- d. Coining
- e. Flame spraying

In hot pressing, the heat and pressure are applied simultaneously while the material is confined in a die or mold. This procedure is commonly used in the formation of articles from plastic materials. In cold pressing and free sintering, the material is pressed in a die at ambient temperature to obtain the desired form and is then removed from the die and subsequently fired in a furnace to develop the final strength. Ceramic materials are commonly formed by this technique. Materials which are too fluid to be pressed can be utilized by casting in an open mold, followed by firing at elevated temperatures either in the mold or after being removed. Ceramics are also prepared by this technique. The fourth method, coining, is used in the formation of metal objects which are ductile and

malleable, and is not applicable to the formation of zeolite membranes. The metal is heated to a semiplastic condition and then quickly pressed or stamped to impart the desired shape and form. Flame spraying is carried out by passing powder particles of a single material or a mixture of materials through a hot flame or a d-c plasma arc. The particle surfaces soften or melt, and they coalesce upon impinging on a target. It might be possible to apply this method to zeolite and binder powder mixtures, provided the zeolite particles' residence time in the hot zone is well controlled so that their physical and chemical properties are not impaired.

All but the fourth of these techniques are applicable to the formation of membranes from mixtures of zeolites and binders. Hot pressing has the advantage of yielding maximum density, but not all mixtures can be handled in this fashion. Much of the work during this quarter has been carried out by casting and firing, since some of the mixtures are initially fluid slurries.

Two special powder compaction dies have been obtained to carry out the pressing of 2.00-in. circular membranes. One was constructed of highly polished Carboloy cemented tungsten carbide, which has been reported to resist galling by the basic zeolites at elevated temperatures and pressures, (Reference 5). The other was constructed of a highly polished Stellite Alloy 6B, a cobalt-based wrought alloy that is reported to be exceptionally strong and to resist acid corrosion.

2.2.2 Inorganic Phosphate Binders

Cations of high charge-to-radius ratio readily react with anionic groups possessing strong coordination tendencies. In these reactions, shared-electron bonds are formed as a result of electron donation by anions and electron acceptance by cations. Bonds of this type are termed "coordinate" or "dative" and are common in chemical reactions involving the cementing or fusing of refractories.

Acid phosphate groups (such as $\text{H}_2\text{PO}_4^{-2}$) have strong electron donor (ligand) properties and, therefore, readily coordinate with cations of periodic groups II and III and the transition element series. If the cations are already incorporated in the coordination compounds, they may still be reacted with acid phosphate groups by applying the Le Chatelier principle, i. e., choosing an ion concentration sufficiently high to appreciably shift the reaction equilibrium in favor of phosphate combination. Thus, when finely divided metal oxides are treated with concentrated phosphoric acid, oxygen atoms are partly displaced by phosphate. On heating, the phosphorylated oxides dehydrate, condensing the acid phosphate groups into linkages between the phosphate tetrahedra. This results in fusion of the mixture into a solid mass. With at least one oxide, ZnO, furnace firing is not required to effect solidification or setting following reaction with acid phosphate. Possibly this is due to the exothermic nature of this particular reaction, the heat required for condensing phosphate groups being self-generated.

Since the bonding of zeolite powders into physically and thermally stable membranes is a prerequisite to the construction of practical zeolite fuel cell wafers, a means was sought to accomplish this task. A convenient and promising approach, but by no means the only one available, appeared to be offered by phosphate bonding reactions, in which cement-like

combinations of metal oxides and acid phosphates would be used to join together the zeolite particles. An experimental program was initiated to test various oxide-phosphate-zeolite mixtures. For preliminary evaluation, three metal oxides were selected: ZrO_2 , Al_2O_3 , and ZnO . These were reacted individually with phosphoric acid and Zeolon H. The procedure employed was as follows:

- a. Predetermined weights of concentrated phosphoric acid, metal oxide, and zeolite were combined in a glass mixing vessel.
- b. Sufficient water was added to the constituents to give a pasty consistency upon mixing.
- c. The slurry was troweled into an open-face Teflon mold 0.030-in. deep.
- d. The material was dried in the mold at about 150°C . After several hours at this temperature, the material acquired sufficient rigidity and strength to be removed in sheet form.
- e. Finally, the dried membrane sheets were fired overnight at 500°C and then cooled in the furnace.

A number of the combinations tested appeared promising with regard to physical strength. Systematic variations were then made with these particular compositions, and the transverse strength of membranes formed from them was measured as described in a following section. These compositions and their respective transverse strengths are given in Table IV in a following section.

2.2.3 Inorganic Silicate Binders

A number of experiments were carried out with various silicate-based proprietary mixtures in order to prepare membranes with a silicate binder. The results, shown in Table II, were unsuccessful. The reportedly adhesive mixtures, such as the Eccoceram or Sauereisen compounds, did not supply bonding strength even at appreciable concentrations. It is possible that a chemical reaction may have occurred between the zeolite and the bonding agents. Various forms of sodium silicate ("STAR" and "GD" designations) were also tested, but no appreciable strength was developed. Some additional work is being planned with silicate binders. The work completed to date, however, is not encouraging.

2.2.4 Organic Binders

Various organic-based binders were evaluated during the report period. All organic binders are electrical insulators, and therefore high concentrations of organic binders cannot be tolerated, since the overall electrical resistivity of the membrane would be increased. An organic binder could be used only if it developed sufficient strength at low concentrations, displayed adequate thermal stability, and did not prevent hydrogen ion transport. Since it has been

TABLE II
EVALUATION OF SILICATE BINDERS

<u>Binder</u>	<u>Mfr.</u>	<u>Zeolite</u>	<u>Preparative Technique</u>	<u>Membrane Strength</u>
20% "STAR" solution	(1)	4A	Hot press	Fragile
10% "GD" powder	(1)	4A	Hot press	Fragile
10% "GD" powder	(1)	4A	Cold press-free sinter	Fragile
10% Eccoceram E-21	(2)	Zeolon H	Cast and fired	No strength
20% Eccoceram E-21	(2)	Zeolon H	Cast and fired	No strength
40% Eccoceram E-21	(2)	Zeolon H	Cast and fired	No strength
10% Sauereisen #30	(3)	Zeolon H	Cast and fired	Weak
20% Sauereisen #30	(3)	Zeolon H	Cast and fired	Weak
40% Sauereisen #30	(3)	Zeolon H	Cast and fired	Weak
10% Eccoceram QC	(2)	Zeolon H	Cast and fired	No strength
20% Eccoceram QC	(2)	Zeolon H	Cast and fired	No strength
40% Eccoceram QC	(2)	Zeolon H	Cast and fired	No strength

- (1) Philadelphia Quartz Co.
(2) Emerson and Cumings, Inc.
(3) Sauereisen Cements Co.

reported (Reference 5) that dry zeolite membranes can be compacted to only 90% of theoretical density, if an organic binder would develop sufficient strength at about 10% concentration, it might only be filling the void spaces and not appreciably affecting the zeolite-to-zeolite particle contact.

The types of organic binders tested and the preparative techniques employed are shown in Table III. A representative cross section of the better-known organic adhesives was tested at low concentrations. Only epoxy type binders showed any promise of developing adequate strength at these concentrations. They also possess a relatively high temperature resistance. The others (Teflon, a polyvinyl chloride, a phenolic, and two types of silicone rubber adhesives) exhibited little or no strength at the concentrations tested. However, only alkaline forms of zeolites have been tested, principal among them being Type 4A. Different results might be obtained with an acidic zeolite, i. e., Zeolon H. Hot pressing, cold pressing and free sintering and casting and firing techniques could be used with various epoxy resins.

No quantitative measure of the strength of these membranes has yet been obtained. An extensive investigation of physical properties has been delayed pending the outcome of investigations of the electrical conductivity. Since epoxy polymers are known to have very high resistivities, the use of epoxy binders may prove deleterious to conductivity. In addition, use of any organic material as a binding agent will impose a limitation on the maximum temperatures at which the membrane can be used and will partially impose the disadvantages of organic membranes. In general, an inorganic type of binder would be preferred for fuel cell applications. Organic binders will receive attention only if inorganic materials are unable to meet the many requirements.

2.3 Physical and Electrochemical Properties of Membranes

2.3.1 Transverse Strength Measurements

Transverse strength measurements were limited to testing phosphate-bonded Norton Zeolon membranes. Silicate-bonded membranes were too weak to test, and strength measurements with epoxy-bonded membranes were deferred pending investigation of their electrochemical properties. Phosphate-bonded Norton Zeolon H compositions exhibiting good physical properties (freedom from cracking, warpage, and surface irregularities) were tested for transverse strength. In this test the breaking strength of the ceramic bodies was measured under flexural stress by means of the apparatus illustrated in Figure 1. Specimens having dimensions of 4 x 1 x 0.030 in. were supported on two rounded knife edges spaced 1.5 in. apart on one pan of a double-beam trip balance. By adding water to a beaker mounted on the opposite pan of the balance at a fixed rate of 45 grams per minute, a load increasing at a constant rate was applied at the center of the membrane. Water flow was stopped at the break point,

TABLE III
EVALUATION OF ORGANIC BINDERS

<u>Binder</u>	<u>Zeolite</u>	<u>Preparative Technique</u>	<u>Membrane Strength</u>
1. <u>Epoxy Resin</u>			
20% Hysol 4314	4A	Hot press	Strong
20% Hysol 4314	4A	Cold press-free sinter	Weak
16% Coraline 530	4A	Hot press	Moderate strength
30% G190/V140	4A	Cast and fired	Strong
15% G190/V140	4A	Cast and fired	Strong
10% G190/V140	4A	Cast and fired	Strong
5% G190/V140	4A	Cast and fired	Strong
10% G190/V140	4A	Cold press-free sinter	Strong
20% G190/V140	4A	Cold press-free sinter	Strong
10% G190/V140	13X	Hot press	Strong
2. <u>Teflon</u>			
10% Teflon	4A	Hot press	No strength
10% Teflon	4A	Cold press-free sinter	No strength
3. <u>Polyvinyl Chloride Resin</u>			
30% Pliovic S-50	4A	Hot press	No strength
4. <u>Phenolic Resins</u>			
30% Durez 1400	4A	Hot press	Fragile
5. <u>Silicone Resins</u>			
20% Eccosil 4712	4A	Hot press	No strength
20% D-C 2105A	4A	Hot press	No strength

and the weight required was determined. From the data obtained, the membrane strength was calculated by the following empirical equation

$$M = \frac{3Wl}{2bh^2}$$

where M is the modulus of rupture (transverse strength) in lb/in.², W is the load in pounds, l is the distance between the knife edges in inches, b is the specimen width in inches, and h is the thickness of the specimen in inches. This equation applies specifically to a rectangular prism and is derived from the more general equation

$$M = \frac{SC}{I}$$

where M is the modulus of rupture, S is the maximum bending moment, C is the distance to the fiber carrying the greatest stress, and I is the moment of inertia.

The general physical properties of the prepared membranes (i. e., qualitative strength and freedom from cracks) are listed in Table IV as a function of chemical composition. All of the membranes were first prepared as disk membranes, 2 in. in diameter and 0.030 in. thick. Those of the membranes that exhibited fair to good physical properties were recast in quadruplicate in the form of rectangular sheets and were subjected to flexural strength testing. The results obtained are listed in Table IV under the heading "Transverse Strength." The standard deviation of the mean ($\sigma_{\bar{x}}$) is indicated by the value after the symbol \pm in the same column*.

From the data in the table, it is apparent that ZrO₂ compositions generally yielded membranes with higher strength properties than did either ZnO or Al₂O₃. For the more promising mixtures of the ternary system containing ZrO₂, a triaxial plot of transverse strength vs composition is shown in Figure 2. The curve connects points corresponding to mixtures having similar transverse strengths. From this curve it is reasonable to draw two general conclusions:

- a. A phosphoric acid content of 33 to 50% appears to be required to obtain membranes of substantial strength (modulus of rupture ~1000 psi).

*Standard deviation of the mean is defined mathematically as

$$\sigma_{\bar{x}} = \sigma / \sqrt{n-1} = \sqrt{\sum (x-\bar{x})^2} / \sqrt{n-1}$$

where σ is the standard deviation, n is the number of observations, x is the value of individual measurements, and \bar{x} is the average value of the separate measurements. The standard deviation of the mean gives the interval within which the true average most probably lies 68% of the time. The 90% probability level is given by 1.64 $\sigma_{\bar{x}}$ and the 99% level by 2.58 $\sigma_{\bar{x}}$.

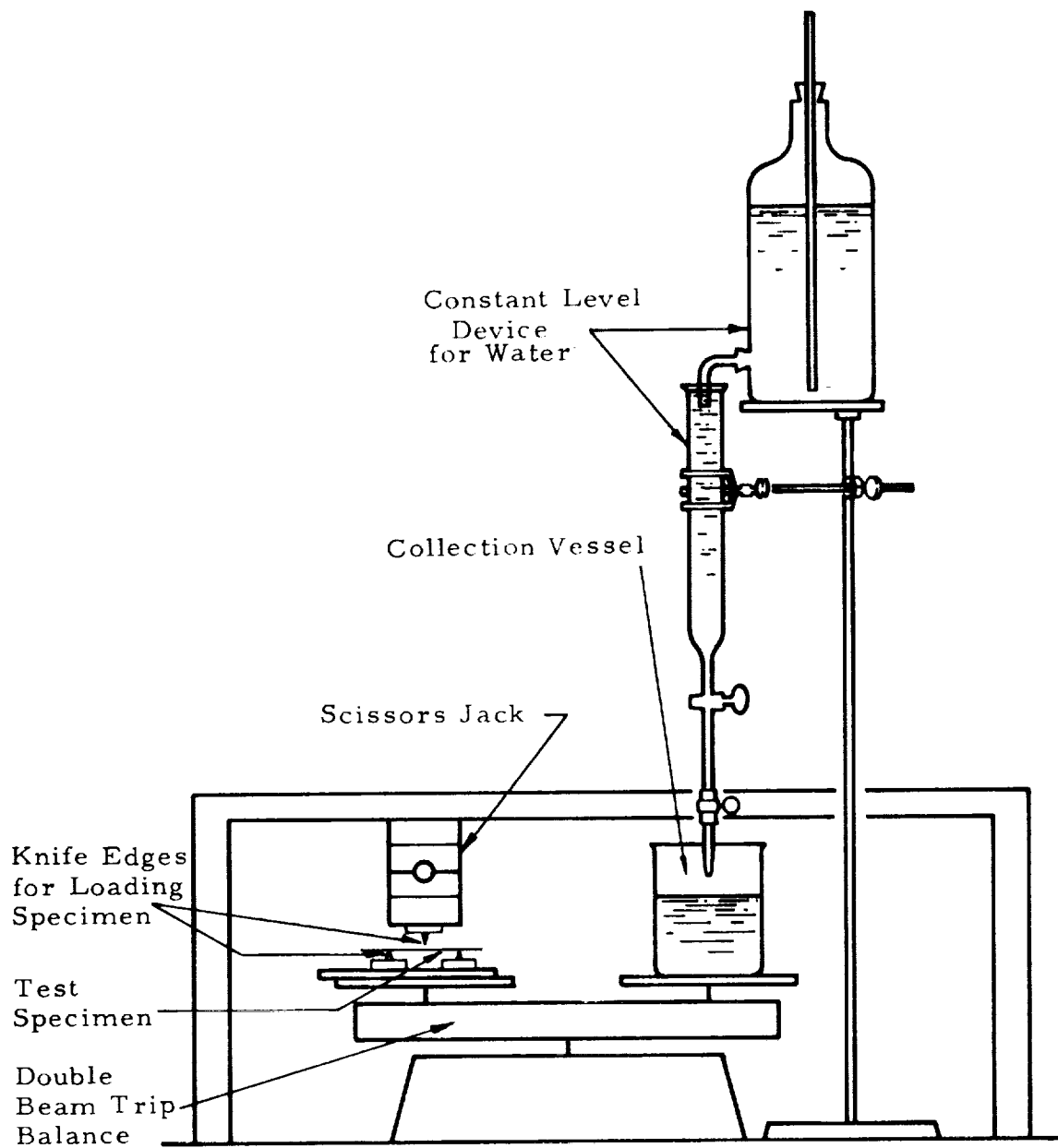


Figure 1. Apparatus for Measuring Transverse Strength of Zeolite Membranes

TABLE IV

PHYSICAL PROPERTIES OF PHOSPHATE-BONDED ZEOLON H

Chemical Composition (Parts by Weight ⁽¹⁾)					General Physical Properties	Transverse Strength ⁽²⁾ (lb/in ²)
Metal Oxide			Zeolon H	Phosphoric Acid (85 w% H ₃ PO ₄)		
Al ₂ O ₃	ZnO	ZrO ₂				
4 3		4	0	2	Poor	N. R. ⁽³⁾
		3	2	1	Poor	N. R.
		3	1	2	Fair	N. R.
		3	0	3	Good	1453±274
		2	4	0	Poor	N. R.
		2	3	1	Poor	N. R.
		2	2	2	Good	1165±154
		2	1	3	Fair	660±47
		2	0	4	Poor	N. R.
		1.5	2.5	2	Good	1095±40
		1.5	2.0	2.5	Good	588±62
		1.5	1.5	3	Poor	N. R.
		1.5	1.0	3.5	Poor	N. R.
		1	3	2	Fair	N. R.
		1	2.5	2.5	Good	1177±67
		1	2	3	Fair	N. R.
		0.5	3	2.5	Poor	N. R.
		0	4	2	Fair	479±76
		4	2	0	Poor	N. R.
		3	2	1	Poor	N. R.
		3	1	2	Poor	N. R.
		2	3	1	Poor	N. R.
		2	2	2	Poor	N. R.
		2	1	3	Fair	N. R.
		2	0	4	Poor	N. R.
		1.5	3.5	1	Fair	N. R.
		1.5	3	1.5	Poor	N. R.
		1.5	2.5	2	Poor	N. R.
		1.5	2	2.5	Poor	N. R.
		1.5	1	3.5	Poor	N. R.
		1	3	2	Fair	515±32
		1	2.5	2.5	Fair	964±59
		1	2	3	Fair	N. R.
		0.5	3	2.5	Good	N. R.
		0.5	2.5	3	Poor	N. R.
			2	0	Poor	N. R.
		2	1	Poor	N. R.	

(1) Total parts = 6

(2) Modulus of rupture

(3) N.R.: Not run

TABLE IV (Continued)

Chemical Composition (Parts by Weight)				General Physical Properties	Transverse Strength (lb/in ²)	
Metal Oxide			Zeolon H			Phosphoric Acid (85 w% H ₃ PO ₄)
Al ₂ O ₃	ZnO	ZrO ₂				
3			1	2	Poor	N. R.
2			3	1	Poor	N. R.
2			2	2	Fair	N. R.
2			1	3	Fair	N. R.
2			0	4	Poor	N. R.
1.5			2.5	2	Fair	N. R.
1.5			2	2.5	Fair	351±75
1.5			1.5	3	Poor	N. R.
1.5			1	3.5	Poor	N. R.
1			3	2	Fair	447±103
1			2.5	2.5	Good	912±83
1			2	3	Fair	N. R.
0.5			3	2.5	Fair	662 (single specimen)

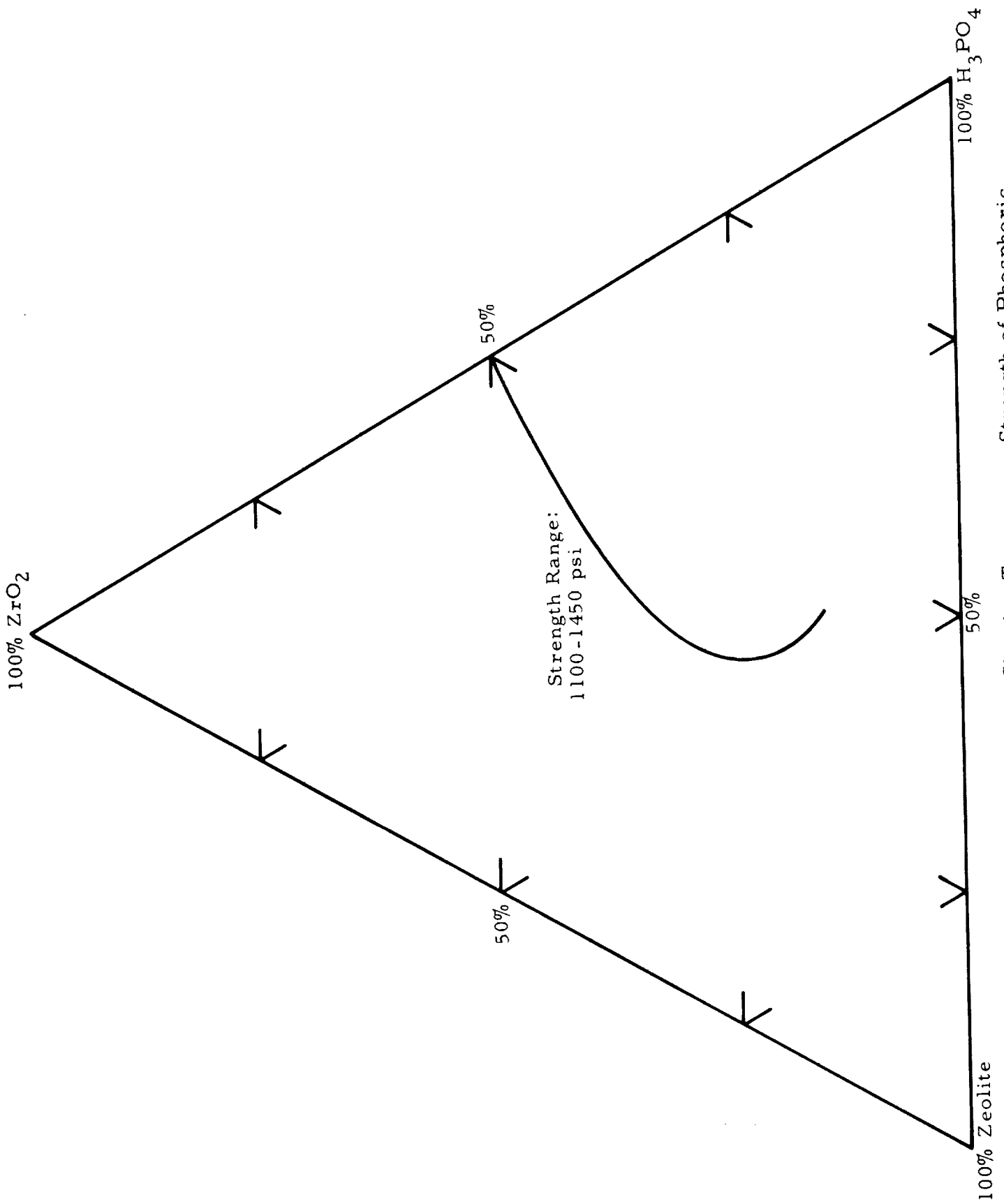


Figure 2. Composition Diagram Showing Transverse Strength of Phosphoric Acid-Zirconium Oxide-Zeolite Mixtures

- b. Considerable latitude exists for varying ZrO_2 /zeolite ratio without ensuing change in membrane strength.

Bonding of zeolites directly by a phosphate-silicate reaction is possible and was demonstrated by mixing two parts by weight of zeolite with four parts by weight of H_3PO_4 . However, the resulting membranes, as noted in Table IV, showed relatively poor breaking strength (479 psi). Evaluation of other binary compositions is planned for the future.

2. 3. 2 Conductivity Measurements

A necessary requirement for the use of zeolite membranes as quasi-solid electrolytes in fuel cells is that they exhibit a low value of electrical resistance, which may be expressed as specific resistivity. The conductivity, or low resistance, should be electrolytic by nature and must result from hydrogen ion transport rather than electronic conduction, since the fuel cell would essentially be internally short-circuited if electronic conduction occurred. An examination of the literature revealed that specific resistivity has been reported for only a few synthetic zeolites (Reference 5). The specific resistivity for Linde zeolites of types A, X, and Y were reported for anhydrous polycrystalline compacts of relatively high density. In view of the limited specific resistivity data available, a very important part of the present investigation involves the screening of a wide variety of hydrated zeolite membranes and composite wafers by means of resistance measurements to evaluate the effect of chemical composition as well as the influence of the physical conditions employed in membrane preparation.

For the measurement of electrical resistance of materials, either direct or alternating current methods may be employed. The measurement of resistance by means of direct current methods proved to be unsuitable for screening zeolite membranes. Preliminary experiments demonstrated that the flow of direct current through zeolite membranes confined between fairly large platinum electrodes is accompanied by large electrode polarization, which results from the electrolysis of water at the electrode-membrane interface and complicates the measurement of the resistance developed across the membrane. A different direct current method would involve immersion of the membrane in a highly conducting solution through which current immersion of the membrane in a highly conducting solution through which current is passed by a pair of electrodes, while another pair of reference electrodes (one on each side of the membrane) is employed to measure the resistance of the membrane. This method is restricted to zeolite membranes containing a single cation, so that the membrane composition will not be altered by the highly conducting solution by means of cation exchange, and is not suitable for use as a screening technique.

On the other hand, the alternating current method was selected for measuring membrane resistance because electrode polarization

quite generally has a small effect on the value of resistance obtained by this method. Moreover, this method possesses the high degree of precision characteristic of bridge measurements, as well as allowing measurements to be taken in a minimum of time.

The alternating current bridge used does not possess capacitance compensation when directly employed to measure membrane resistance; however, a good null was obtained with a variety of membranes investigated. To assure that the impedance measured represents pure resistance, this bridge was employed to measure capacity and storage factor of the same membrane, allowing the membrane resistance to be calculated. Satisfactory agreement of the resistance for a given membrane was obtained by these two procedures at a number of different frequencies of alternating current.

As deduced from preliminary measurements, the degree of hydration of the membrane is an important variable in resistance measurements. In order to simplify the screening process, it was therefore decided to make all the initial measurements on membranes with a 100% relative humidity atmosphere at 25°C. A schematic diagram of the apparatus employed is shown in Figure 3. This experimental method was designed to measure membrane as well as composite wafer resistance and is particularly suited for measurements in the temperature range from 25° to 70°C. However, suitable modifications are being planned for measurements on promising membranes at 115°C or above after the screening work is completed.

The present experimental apparatus consists of a screw assembly, a bell jar, a regulated water bath, and electronic instrumentation for alternating current bridge measurements. By means of a screw assembly, the zeolite membrane under investigation is sandwiched between two cylindrical stainless steel electrodes (2.47 cm²) which are expected to provide adequate electrical contact under pressure with the zeolite membrane. In order to control the temperature and the saturated water vapor pressure in contact with the membrane contained in the screw assembly, the latter is mounted in a bell jar immersed in a regulated water bath. This provides a closed system in which the temperature and vapor pressure of water vapor are determined by the temperature of the water bath.

The bridge employed for alternating current measurements was an Electro-Measurements, Inc. impedance bridge No. 290R in conjunction with an a-c generator-detector No. 860R. In order to improve detection of bridge balance, a Tektronix oscilloscope Type 543A was employed as a null detector after preamplification by means of a Hewlett Packard Model 400D vacuum tube volt meter.

Experimental values for the resistance of membranes will be presented in detail in the next quarterly progress report, due to the need for establishing the effects of membrane history, chemical composition, and homogeneity of

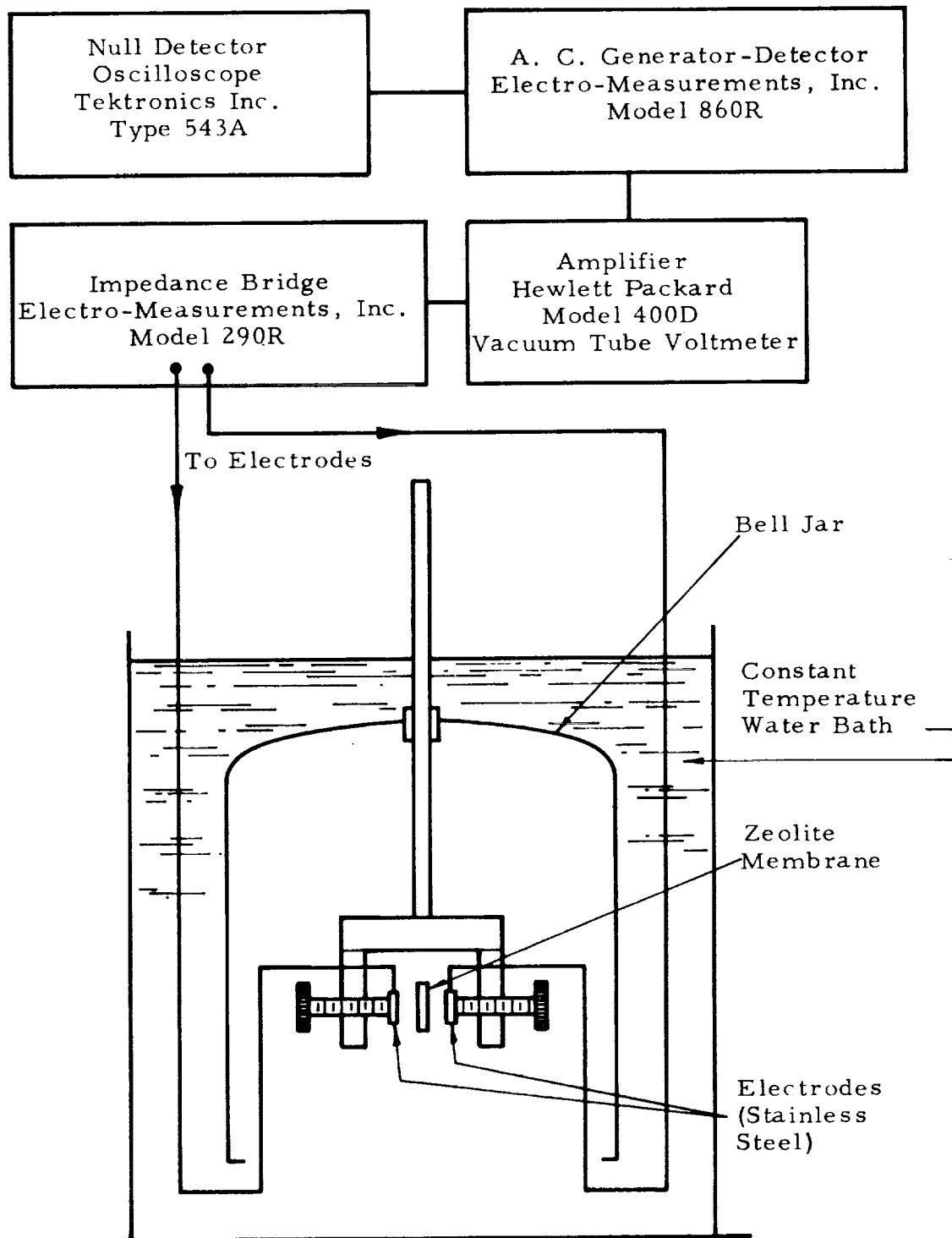


Figure 3. Schematic of Apparatus for Measurement of Specific Resistivity of Membranes at Various Saturated Vapor Pressures of Water

membrane, as well as other physical variables, before reporting meaningful values for membrane resistance.

2.3.3 Diffusion Measurements

In order to operate satisfactorily in an actual fuel cell, the membrane should not permit significant amounts of reactant diffusion to occur between the fuel and oxidizer electrode. Potentially explosive mixture, could be formed; in addition, any gas which passes through the membrane without undergoing an electrochemical reaction is wasted, and the efficiency of the fuel cell is correspondingly decreased. It is therefore important that the molecular permeability of the various reactants be established as soon as the physical strength and conductivity of various membranes are shown to be promising.

A method of measuring permeability was needed which would allow a preliminary measurement of the amount of gas diffusion through the membrane. Since the permeability will be a function of both the membrane composition and the method of formation, and also may vary somewhat with individual specimens, a relatively large number of tests will have to be carried out. It was therefore necessary to devise a rapid, screening-type method to obtain permeability data.

Evaluation of a water permeability test is underway. The test is essentially a modification of the ASTM moisture vapor permeability test (ASTM designation D1654-59T). In that test, a sample of an organic film is placed over a cup filled with water. Thus any water vapor that leaves the cup must exit through the film. The assembled cup is placed in a dessicator over P_2O_5 to establish a constant, low partial pressure of water vapor on the other side of the film. The cup is periodically removed from the dessicator and weighed to measure the water loss, which is used to calculate the specific permeability. The test has been modified to permit testing of the two-in. diameter membranes prepared in this project.

It is possible that the water permeability of these zeolite membranes may be somewhat different than the gas diffusibility. It is difficult to predict whether a polar molecule such as water vapor, which is strongly adsorbed in the zeolite cavities, would diffuse more or less rapidly than a nonpolar gas such as hydrogen, unless the hydrogen diffuses through intercrystalline pores. Also, the degree of hydration will probably have a marked effect on the diffusion of a gas through a membrane. It is known that the adsorption of water on the zeolites sharply limits the amount of gases which can subsequently be adsorbed (Reference 3).

Despite these uncertainties, however, the measurement of permeability to water vapor should be adequate to reveal the presence of microcracks or faults in the prepared membranes. Once a preliminary selection of the more promising wafer compositions has been made, a

measurement of the diffusion of hydrogen through actual membranes and composite wafers will probably be undertaken. This will involve a more complex and sophisticated vacuum apparatus and would not be suitable for quick screening measurements.

3.0 FUTURE WORK

Substantial advancement will be made during the next quarter toward the goals initially defined in the proposal. Procedures and methods for the initial screening tests have already been defined, and the equipment, for the most part, has been assembled. It is expected that early in the second quarter a selection of the most suitable binder or binders will be made. This selection will, of course, depend upon the physical and electrochemical properties of the resulting membrane. As soon as a general type of binder is chosen, then research can be directed in a more discriminatory direction to optimize the composition and method of formation of the membrane.

After the more suitable membranes have been selected, methods for the addition of powdered catalysts and wire screens to form the completed wafer will be investigated. A certain amount of exploratory experimentation will be required to find a technique that will allow the integration of powder or film catalysts and screens (to act as electrical collectors) with the membrane so that good adhesion and electrical contact are achieved without sealing the zeolite intracrystalline pores. Techniques such as compression of the powdered catalyst and wire screen onto a previously formed membrane at elevated temperatures and pressures, flame spraying of powdered catalyst onto the membrane from a plasma "gun," and printing a metallic layer onto the membrane by methods analogous to those used in printed circuit technology, will be evaluated.

Hydrogen ion exchange with the Linde zeolites will have to be accomplished on the completed membrane. It is reported that the zeolite crystal structure cannot be maintained in the complete hydrogen cation form in the dry condition (Reference 6). The structure collapses irreversibly to other alumina-silicate forms. However, the hydrogen ion exchange does not have to be carried to completion. In addition, the Linde zeolites are not stable in strong acidic solutions; therefore, the exchange into the hydrogen ion will have to be carried out in very weakly acidic solutions. The technique will probably be simply to soak the assembled wafer in a dilute or slightly acidic solution to effect the exchange (Reference 7). Since the Norton zeolite is already supplied in a hydrogen ion form, these problems would not be encountered in utilizing it.

The water adsorption equilibrium must be measured at various temperatures and partial pressures of water vapor. The data may be presented as isotherms or isosteres. Papers have been published describing the apparatus used in measuring the water adsorption properties of some of the Linde zeolites (References 3 and 6). A similar apparatus will be constructed to measure the adsorption of various membranes and of completed wafers.

Measurement of the electrical conductivity has been discussed in detail in preceeding sections. The apparatus to measure resistivity of various membranes at 25°C and 100% relative humidity has been constructed, and considerable data will be collected during the coming quarter.

To date not much attention has been directed toward chemical stability of the membranes or wafers. Investigation of this problem will be deferred until the third quarter. After specific membranes and wafer compositions have been selected, the known chemical reactions and stabilities of the constituents will be examined. Reactions between the catalysts and the zeolites or binders may be one of the significant problems. However, it is planned to use noble metal catalysts, since in such wafers only a relatively small amount is needed.

Measurement of diffusion characteristics has also been discussed in a preceeding section. Water permeability data will be collected during the next quarter for a number of zeolite membranes. A number of multiple tests of the same composition will be carried out to determine the reproducibility of the method and of the membrane formation techniques. It may be found necessary to measure hydrogen diffusion through a selected number of membranes or wafers.

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